

## PATENT ABSTRACTS OF JAPAN

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H01M 10/40

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LTD

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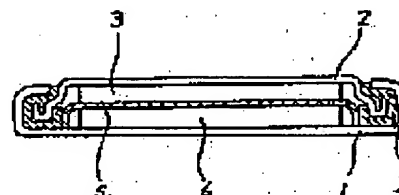
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## (54) ORGANIC ELECTROLYTIC SECONDARY BATTERY

## (57)Abstract:

PURPOSE: To provide a highly reliable organic electrolytic secondary battery.

CONSTITUTION: This secondary battery has a negative electrode 3 consisting of a carbon material capable of storing and releasing lithium, a positive electrode 6, and an organic electrolyte consisting of a solvent and a solute. A mixture of a dioxide thiophene and an acyclic sulfone is used as the solvent. Thus, the reduction in discharge capacity accompanying the progress of charge and discharge cycle which is a problem of batteries of this kind can be effectively suppressed.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The organic electrolytic-solution rechargeable battery which is a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, and is characterized by the aforementioned solvent containing the dioxide thiophene and the un-annular sulfone.

[Claim 2] The organic electrolytic-solution rechargeable battery according to claim 1 which is more than a kind as which a dioxide thiophene is chosen from a sulfolane and 3-methyl sulfolane.

[Claim 3] The organic electrolytic-solution rechargeable battery according to claim 1 or 2 whose un-annular sulfone is one or more sorts chosen from a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the lithium cell which is the high-energy density as the power supply for a drive or memory maintenance power supply of electronic equipment, and has high reliability.

[0002]

[Description of the Prior Art] With the formation of small lightweight with rapid electronic equipment, to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which repeat charge and discharge are still more possible is increasing. As a rechargeable battery which fills these demands, an organic electrolytic-solution rechargeable battery is the most promising.

[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of an organic electrolytic-solution rechargeable battery. Especially, since [ more than 4V (Li/Li+) ] charge and discharge are extremely performed by electropositive potential, a lithium cobalt multiple oxide (LiCoO<sub>2</sub>) and a spinel type lithium manganic acid ghost (LiMnO<sub>4</sub>) can realize the cell which has high discharge voltage by using these as a positive electrode.

[0004] As for the negative-electrode active material of an organic electrolytic-solution rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] However, in this seed cell, while making into a negative-electrode active material the lithium which has \*\*\*\* potential, in order to use the metallic oxide which has electropositive potential, it is in the situation that the electrolytic solution is easy to be decomposed in a negative electrode and each positive electrode in a positive electrode. Therefore, in selection of the electrolytic solution, it is indispensable to consider as the composition in consideration of these points, and using the various electrolytic solutions is proposed.

[0006] For example, the electrolytic solution (refer to JP,4-152879,A) containing the solvent containing S-O combination, the mixed electrolytic solution (refer to JP,4-171674,A) of annular carbonate and chain-like carbonate, etc. are raised.

[0007] On the other hand, generally as a solute, the lithium perchlorate, the trifluoromethane sulfonic-acid lithium, the 6 fluoride [ phosphoric acid ] lithium, etc. are used. A 6 fluoride [ phosphoric acid ] lithium is briskly used increasingly especially in recent years from the reason the ion conductivity of the electrolytic solution in which safety made it dissolve highly is high.

[0008] However, in the dimethyl ape fight which is a solvent containing S-O combination, a dimethyl sulfone, and dimethyl sulfoxide, when the carbon material in which the occlusion and discharge of a lithium are possible was used for the cell used for the negative electrode, in no cases, the good charge-and-discharge cycle property was acquired. Service capacity became small although the sulfolane and 3-methyl sulfolane showed the good charge-and-discharge cycle property. On the other hand, under the room temperature, although the mixed electrolytic solution of annular carbonate and un-annular carbonate showed the good cycle property, under the elevated temperature, the problem that degradation became large produced it.

[0009]

[Means for Solving the Problem] this invention is a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, and the above-mentioned problem is solved by using the mixture of a dioxide thiophene and an un-annular sulfone for the aforementioned solvent at least.

[0010] In addition, in order to obtain the cell which is excellent in a high-rate-discharge performance, it is desirable to use a sulfolane and a 3-methyl-sulfolane as a dioxide thiophene compound, and to use a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone as an un-annular sulfone.

[0011]

[Function] As mentioned above, by this seed cell, it is easy to produce the decomposition reaction of the electrolytic solution, and has become the main factor to which this degrades a cell performance. However, when the mixed solvent of a dioxide thiophene and an un-annular sulfone was used for the electrolytic solution, it excelled in the preservation property, and a cycle property also finds out that a good cell is obtained and came to complete this invention. This reason is guessed as following, although it is not clear.

[0012] Since it is small compared with the molecule of ring compounds, such as a sulfolane and 3-methyl sulfolane, the molecule of a dimethyl aprotic solvent, a dimethyl sulfone, and dimethyl sulfoxide is easy to be incorporated between the layers of negative-electrode carbon with a lithium ion at the time of charge. The distance between layers of negative-electrode carbon is pushed up by it. Therefore, destruction of the layer structure of negative-electrode carbon progresses as the occlusion and discharge of the lithium ion by charge and discharge are repeated, and it is thought that cell capacity fell. Therefore, these solvents were inapplicable to the cell which used the carbon material as a negative electrode. It was difficult to use independently on the other hand, since hyperviscous solvents, such as a sulfolane and 3-methyl sulfolane, have the low ion conductivity of the electrolytic solution. However, if a dioxane thiophene and the un-annular sulfone represented by the dimethyl sulfone were mixed, in order that a dioxane thiophene might form the protective film of lithium ion conductivity in a negative-electrode carbon front face and might suppress incorporation of a lithium ion between [ the negative-electrode carbon layers of an un-annular sulfone molecule ], even if it repeated a charge-and-discharge cycle, it was hard coming to generate destruction of the layer structure of negative-electrode carbon. Furthermore, since the viscosity of the electrolytic solution fell and ion conductivity improved compared with the electrolytic solution using independent solvents, such as a sulfolane and 3-methyl sulfolane, polarization of a cell became small and the cell capacity found cell capacity greatly by leaps and bounds.

[0013] However, the stabilization effect by this protective film is seen only in un-annular sulfones, such as a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone, and the effect was not seen in the specific dimethyl aprotic solvent which has the same S-O combination, and dimethyl sulfoxide. Although this reason is not clear, since a dimethyl aprotic solvent and dimethyl sulfoxide are molecules smaller than a dimethyl sulfone, it tends to pass a protective film and can consider that it is easy to react with a negative-electrode carbon material etc. Furthermore, compared with the mixed electrolytic solution of the annular carbonate and chain-like carbonate which are the conventional electrolytic solution, the charge-and-discharge cycle property of the electrolytic solution of this invention under an elevated temperature is improving. This is considered to originate in not containing the chain-like carbonate inferior to the stability under an elevated temperature.

[0014]

[Example] Although this invention is explained below using a suitable example, unless the meaning of this invention is exceeded, it is not limited to the following examples.

[0015] A positive electrode carries out pressurization molding, after mixing enough the carbon powder as a lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ) and an electric conduction agent, and the fluororesin powder as a binder by the weight ratio of 90:3:7. A negative electrode carries out pressurization molding, after mixing a graphite powder and the fluororesin powder as a binder enough by the weight ratio of 91:9.

[0016] Drawing 1 is drawing of longitudinal section of the example cell of this invention. It is the obturation board which serves as the negative-electrode terminal into which the case which serves as the positive-electrode terminal which 1 pierced the stainless steel plate of electrolytic-solution-proof nature, and was processed in this drawing, and the stainless steel plate as 1 with 2 [ same ] were pierced and processed, and the negative electrode 3 is contacted by the wall. The separator which consists of polypropylene into which 5 sank the organic electrolytic solution, and 6 are positive electrodes. The cell is carrying out sealing obturation by binding tight the periphery of the obturation board 2 which serves as a negative-electrode terminal the opening edge of the case 1 which serves as a positive-electrode terminal through a caulking and a gasket 4 to the inner direction.

[0017] What dissolved the 6 fluoride [ phosphoric acid ] lithium in the organic solvent which mixed the sulfolane and the dimethyl sulfone by the volume ratio 1:1 by the concentration of one mol/l. was used for the organic electrolytic solution. It did about 150microl pouring in of the above-mentioned electrolytic solution at the cell.

[0018] This cell size is 2mm in the diameter of 20mm, and height. this invention cell was set to (A). In the above-mentioned example, everything but having used the ethyl methyl sulfone and the diethyl sulfone instead of the dimethyl sulfone, respectively set to (B) and (C) the cell of this invention considered as the same composition as this example.

[0019] Everything but furthermore having used the mixture (volume ratio 1:1) of ethylene carbonate and diethyl carbonate for comparison made a (a) the comparison cell considered as the same composition as the cell of this invention.

[0020] Next, it is 300 cycle \*\*\*\*\* about the charge-and-discharge cycle-life examination which discharges until it charges these cells by the 2.0mA constant current until terminal voltage results in 4.2V, and it continues and terminal voltage similarly amounts to 2.7V in a 2.0mA constant current in a thermostat with a temperature of 60 degrees C. Change of the service capacity accompanying advance of the charge-and-discharge cycle of each cell is shown in drawing 2.

[0021] this invention cell (A) using the mixed solvent of a dioxane thiophene and an un-annular sulfone, (B), and (C) have the small fall of the service capacity accompanying advance of a charge-and-discharge cycle compared with a comparison cell (a) so that clearly from the result of drawing 2.

[0022] In addition, although the above-mentioned example explained the case where a sulfolane was used as a dioxane thiophene, the mixed solvent of 3-methyl sulfolane, a sulfolane, and 3-methyl sulfolane can be used.

[0023] Although the above-mentioned example explained the case where a dioxane thiophene and an un-annular sulfone were mixed by the volume ratio 1:1, it is not limited especially.

[0024] The addition to the dioxide thiophene of these un-annular sulfones has desirable 10 – 60 volume % to both total amount. Because, when using a sulfolane with the congealing point high when the content of an un-annular sulfone is under 10 volume %, and it becomes easy to solidify the electrolytic solution at low temperature and the content of a sulfone compound with a low dielectric constant exceeds 60 volume % on the other hand, it is for the ion conductivity of the electrolytic solution to fall.

[0025] Moreover, as a sulfone compound used by this invention, although at least one or more sorts, such as a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone, can be used, for example, a dimethyl sulfone is the point of ion conductivity and an ethyl methyl sulfone is the most desirable especially in respect of low-temperature-performance ability.

[0026] Although the case where a lithium cobalt multiple oxide was used as a positive active material was furthermore explained in the above-mentioned example, it is not limited especially. Various things, such as manganese dioxide including 2 titanium sulfides and a lithium nickel multiple oxide ( $\text{LiCoO}_2$ ), a spinel type lithium manganic acid ghost, a vanadium pentoxide ( $\text{LiMnO}_4$ ), and a molybdenum trioxide, can be used.

[0027] Although this example explained the case where the mixed stock of a dioxide thiophene and an un-annular sulfone compound was used for an organic solvent, it can add as a third component and the organic solvent conventionally used with the lithium cell can be used. For example, chain-like carbonate, such as ether solvents, such as annular carbonate solvents, such as ester solvents, such as gamma-butyrolactone and a methyl fall mate, and ethylene carbonate, 1, 2-dimethoxyethane, and a tetrahydro furan, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate, etc. is raised.

[0028] As an electrolyte, one or more sorts, such as a lithium perchlorate, a 6 fluoride arsenic-acid lithium, 4 fluoride lithium borate, a trifluoromethane sulfonic-acid lithium, and a fluosulfonic-acid lithium, can be used.

[0029] In addition, although each cell concerning the aforementioned example is a coin form cell, the same effect is acquired even if it applies this invention to a cylindrical shape, a square shape, or a paper form cell.

[0030]

[Effect of the Invention] As mentioned above, in a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, the fall of the service capacity accompanying advance of the charge-and-discharge cycle which is the problem of this seed cell can be effectively suppressed by using the mixture of a dioxide thiophene and an un-annular sulfone for the aforementioned solvent, and the industrial value is size very much.

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**TECHNICAL FIELD**

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[Industrial Application] this invention relates to the lithium cell which is the high-energy density as the power supply for a drive or memory maintenance power supply of electronic equipment, and has high reliability.

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## EXAMPLE

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[0025] Moreover, as a sulfone compound used by this invention, although at least one or more sorts, such as a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone, can be used, for example, a dimethyl sulfone is the point of ion conductivity and an ethyl methyl sulfone is the most desirable especially in respect of low-temperature-performance ability.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] As mentioned above, in a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, the fall of the service capacity accompanying advance of the charge-and-discharge cycle which is the problem of this seed cell can be effectively suppressed by using the mixture of a dioxide thiophene and an un-annular sulfone for the aforementioned solvent, and the industrial value is size very much.

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## TECHNICAL PROBLEM

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[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of an organic electrolytic-solution rechargeable battery. Especially, since [ more than 4V (Li/Li+) ] charge and discharge are extremely performed by electropositive potential, a lithium cobalt multiple oxide (LiCoO<sub>2</sub>) and a spinel type lithium manganic acid ghost (LiMnO<sub>4</sub>) can realize the cell which has high discharge voltage by using these as a positive electrode.

[0004] As for the negative-electrode active material of an organic electrolytic-solution rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] However, in this seed cell, while making into a negative-electrode active material the lithium which has \*\*\*\* potential, in order to use the metallic oxide which has electropositive potential, it is in the situation that the electrolytic solution is easy to be decomposed in a negative electrode and each positive electrode in a positive electrode. Therefore, in selection of the electrolytic solution, it is indispensable to consider as the composition in consideration of these points, and using the various electrolytic solutions is proposed.

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[0007] On the other hand, generally as a solute, the lithium perchlorate, the trifluoromethane sulfonic-acid lithium, the 6 fluoride [ phosphoric acid ] lithium, etc. are used. A 6 fluoride [ phosphoric acid ] lithium is briskly used increasingly especially in recent years from the reason the ion conductivity of the electrolytic solution in which safety made it dissolve highly is high.

[0008] However, in the dimethyl ape fight which is a solvent containing S-O combination, a dimethyl sulfone, and dimethyl sulfoxide, when the carbon material in which the occlusion and discharge of a lithium are possible was used for the cell used for the negative electrode, in no cases, the good charge-and-discharge cycle property was acquired. Service capacity became small although the sulfolane and 3-methyl sulfolane showed the good charge-and-discharge cycle property. On the other hand, under the room temperature, although the mixed electrolytic solution of annular carbonate and un-annular carbonate showed the good cycle property, under the elevated temperature, the problem that degradation became large produced it.

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## OPERATION

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[Function] As mentioned above, by this seed cell, it is easy to produce the decomposition reaction of the electrolytic solution, and has become the main factor to which this degrades a cell performance. However, when the mixed solvent of a dioxide thiophene and an un-annular sulfone was used for the electrolytic solution, it excelled in the preservation property, and a cycle property also finds out that a good cell is obtained and came to complete this invention. This reason is guessed as following, although it is not clear. [0012] Since it is small compared with the molecule of ring compounds, such as a sulfolane and 3-methyl sulfolane, the molecule of a dimethyl ape fight, a dimethyl sulfone, and dimethyl sulfoxide is easy to be incorporated between the layers of negative-electrode carbon with a lithium ion at the time of charge. The distance between layers of negative-electrode carbon is pushed up by it. Therefore, destruction of the layer structure of negative-electrode carbon progresses as the occlusion and discharge of the lithium ion by charge and discharge are repeated, and it is thought that cell capacity fell. Therefore, these solvents were inapplicable to the cell which used the carbon material as a negative electrode. On the other hand, hyperviscous solvents, such as a sulfolane and 3-methyl sulfolane, were difficult for the ion conductivity of the electrolytic solution using independently for a low reason. However, if a dioxide thiophene and the un-annular sulfone represented by the dimethyl sulfone were mixed, in order that a dioxide thiophene might form the protective film of lithium ion conductivity in a negative-electrode carbon front face and might suppress the incorporation of a between [ the negative-electrode carbon layers of an un-annular sulfone molecule ], even if it repeated a charge-and-discharge cycle, it was hard coming to generate destruction of the layer structure of negative-electrode carbon. Furthermore, since the viscosity of the electrolytic solution fell and ion conductivity improved compared with the electrolytic solution using independent solvents, such as a sulfolane and 3-methyl sulfolane, polarization of a cell became small and the bird clapper found cell capacity greatly by leaps and bounds.

[0013] However, the stabilization effect by this protective film is seen only in un-annular sulfones, such as a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone, and the effect was not seen in the specific dimethyl ape fight which has the same S-O combination, and dimethyl sulfoxide. Although this reason is not clear, since a dimethyl ape fight and dimethyl sulfoxide are molecules smaller than a dimethyl sulfone, it tends to pass a protective film and can consider that it is easy to react with a negative-electrode carbon material etc. Furthermore, compared with the mixed electrolytic solution of the annular carbonate and chain-like carbonate which are the conventional electrolytic solution, the charge-and-discharge cycle property of the electrolytic solution of this invention under an elevated temperature is improving. This is considered to originate in not containing the chain-like carbonate inferior to the stability under an elevated temperature.

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**MEANS**

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[Means for Solving the Problem] this invention is a cell equipped with the negative electrode which consists of a carbon material in which the occlusion and discharge of a lithium are possible, a positive electrode, and the organic electrolytic solution which consists of a solvent and a solute, and the above-mentioned problem is solved by using the mixture of a dioxide thiophene and an un-annular sulfone for the aforementioned solvent at least.

[0010] In addition, in order to obtain the cell which is excellent in a high-rate-discharge performance, it is desirable to use a sulfolane and a 3-methyl-sulfolane as a dioxide thiophene compound, and to use a dimethyl sulfone, an ethyl methyl sulfone, and a diethyl sulfone as an un-annular sulfone.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the internal structure of the button cell which is an example of an organic electrolytic-solution rechargeable battery.

[Drawing 2] It is the table having shown change of the service capacity accompanying advance of the charge-and-discharge cycle of an examination cell.

[Description of Notations]

- 1 Cell Case
- 2 Obturation Board
- 3 Negative Electrode
- 4 Gasket
- 5 Separator
- 6 Positive Electrode

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[Translation done.]

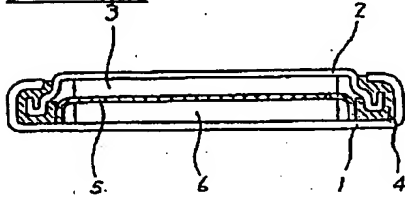
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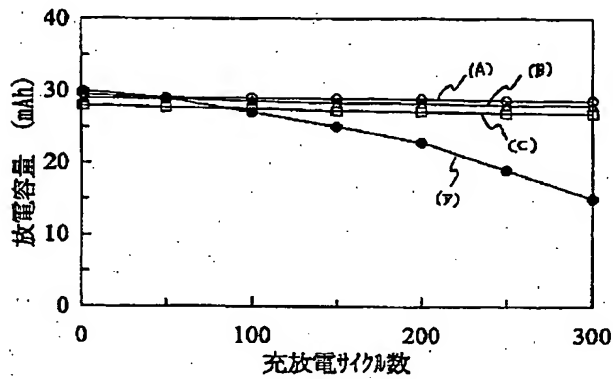
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- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

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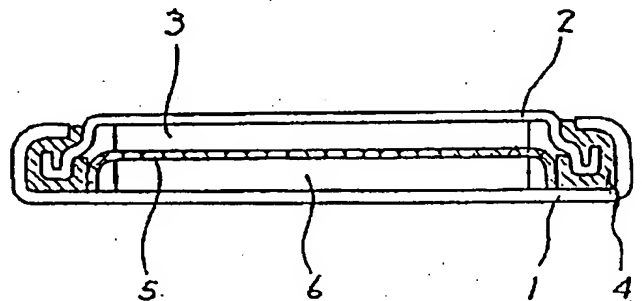
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(54) 【発明の名称】 有機電解液二次電池

(57) 【要約】

【目的】 信頼性の高い有機電解液二次電池を提供する。

【構成】 リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池において、前記溶媒にジオキシドチオフェンと非環状スルホンとの混合物を用いることで、この種電池の問題である充放電サイクルの進行にともなう放電容量の低下を有効に抑制できる。



(2)

## 【特許請求の範囲】

【請求項1】リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池であって、前記溶媒がジオキシドチオフェンと非環状スルホンとを含有していることを特徴とする有機電解液二次電池。

【請求項2】ジオキシドチオフェンがスルホラン、3-メチルスルホランから選ばれる一種以上である請求項1記載の有機電解液二次電池。

【請求項3】非環状スルホンが、ジメチルスルホン、エチルメチルスルホン、ジエチルスルホンから選ばれる1種以上である請求項1または2記載の有機電解液二次電池

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、電子機器の駆動用電源もしくはメモリ保持電源としての高エネルギー密度でかつ高い信頼性を有するリチウム電池に関するものである。

## 【0002】

【従来の技術とその課題】電子機器の急激なる小形軽量化に伴い、その電源である電池に対して小形で軽量かつ高エネルギー密度で、更に繰り返し充放電が可能な二次電池の開発への要求が高まっている。これら要求を満たす二次電池として、有機電解液二次電池が最も有望である。

【0003】有機電解液二次電池の正極活物質には、二硫化チタンをはじめとして、リチウムコバルト複合酸化物、スピネル型リチウムマンガン酸化物、五酸化バナジウムおよび三酸化モリブデンなどの種々のものが検討されている。なかでも、リチウムコバルト複合酸化物 ( $\text{LiCoO}_2$ ) およびスピネル型リチウムマンガン酸化物 ( $\text{LiMnO}_4$ ) は、4V ( $\text{Li}^+/\text{Li}^+$ ) 以上のきわめて貴な電位で充放電を行うため、これらを正極として用いることで高い放電電圧を有する電池が実現できる。

【0004】有機電解液二次電池の負極活物質は、金属リチウムをはじめとしてリチウムの吸蔵・放出が可能な  $\text{Li}-\text{Al}$  合金や炭素材料など種々のものが検討されているが、なかでも炭素材料は、安全性が高くかつサイクル寿命の長い電池が得られるという利点がある。

【0005】しかし、この種電池において、卑な電位を有するリチウムを負極活物質とする一方、正極では貴な電位を有する金属酸化物を用いるため、負極、正極それぞれにおいて電解液が分解されやすい状況にある。従って、電解液の選択において、これらの点を考慮した構成とすることが必要不可欠であり、種々の電解液を用いることが提案されている。

【0006】例えば、 $\text{S}-\text{O}$ 結合を含有する溶媒を含有する電解液（特開平4-152879号公報参照）や環状カーボネートと鎖状カーボネートとの混合電解液（特

開平4-171674号公報参照）などがあげられる。

【0007】一方、溶質としては、過塩素酸リチウム、トリフルオロメタンスルホン酸リチウム、六フッ化リン酸リチウムなどが一般に用いられている。なかでも六フッ化リン酸リチウムは、安全性が高くかつ溶解させた電解液のイオン導電率が高いという理由から、近年盛んに用いられるようになってきている。

【0008】しかしながら、 $\text{S}-\text{O}$ 結合を含有する溶媒であるジメチルスルファイト、ジメチルスルホン、ジメチルスルホキシドを、リチウムの吸蔵・放出が可能な炭素材料を負極に用いた電池に使用したところ、全ての場合において良好な充放電サイクル特性が得られなかった。スルホランおよび3-メチルスルホランは、良好な充放電サイクル特性を示すが、放電容量が小さくなった。一方、環状カーボネートと非環状カーボネートとの混合電解液は、室温下では良好なサイクル特性をしめすものの、高温下では劣化が大きくなるという問題が生じた。

## 【0009】

【課題を解決するための手段】本発明は、リチウムの吸蔵・放出が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池であって、前記溶媒に少なくともジオキシドチオフェンと非環状スルホンとの混合物を用いることで上記問題を解決するものである。

【0010】なお、高率放電性能に優れる電池を得るには、ジオキシドチオフェン化合物としてスルホランおよび3-メチルスルホランを、非環状スルホンとしてジメチルスルホン、エチルメチルスルホンおよびジエチルスルホンを用いるのが好ましい。

## 【0011】

【作用】前述した如く、この種電池では電解液の分解反応が生じやすく、これが電池性能を劣化させる主因となっている。しかしながら、電解液にジオキシドチオフェンと非環状スルホンとの混合溶媒を用いると、保存特性に優れ、サイクル特性も良好な電池が得られることを見出し、本発明を完成するに至った。この理由は明らかではないが下記の如く推察している。

【0012】ジメチルスルファイト、ジメチルスルホン、ジメチルスルホキシドの分子は、スルホラン、3-メチルスルホランなどの環状化合物の分子に比べ小さいため、充電時にリチウムイオンとともに負極炭素の層間に取り込まれやすい。それによって負極炭素の層間距離が押し上げられる。したがって、充放電によるリチウムイオンの吸蔵・放出を繰り返すにつれて負極炭素の層構造の破壊が進み、電池容量が低下したと考えられる。故に、これら溶媒は、炭素材料を負極として用いた電池に適用できなかった。一方、スルホランおよび3-メチルスルホランなどの高粘度溶媒は、電解液のイオン導電率が低いと単独で用いることは困難であった。ところ



(3)

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が、ジオキシドチオフェンとジメチルスルホンに代表される非環状スルホンとを混合すると、ジオキシドチオフェンが負極炭素表面にリチウムイオン導電性の保護皮膜を形成し、非環状スルホン分子の負極炭素層間への取り込みを抑制するため、充放電サイクルを繰り返しても負極炭素の層構造の破壊が生じにくくなった。さらに、スルホラン、3-メチルスルホランなどの単独溶媒を用いた電解液に比べて、電解液の粘度が低下し、イオン導電率が向上するため電池の分極が小さくなり電池容量が飛躍的に大きくなることがわかった。

【0013】しかし、この保護皮膜による安定化効果は、ジメチルスルホン、エチルメチルスルホン、ジエチルスルホンなどの非環状スルホンにおいてのみ見られる特異的なもので、同じS-O結合を有するジメチルスルファイト、ジメチルスルホキシドでは、効果は見られなかった。この理由は、明らかではないが、ジメチルスルファイト、ジメチルスルホキシドは、ジメチルスルホンよりも小さい分子であるため、保護皮膜を通過しやすく、負極炭素材料と反応しやすいことなどが考えられる。さらに、本発明の電解液は、従来の電解液である環状カーボネートと鎖状カーボネートとの混合電解液に比べて、高温下での充放電サイクル特性が向上している。これは、高温下での安定性に劣る鎖状カーボネートを含

【0014】

【実施例】以下に、好適な実施例を用いて本発明を説明するが、本発明の趣旨を越えない限り、以下の実施例に限定されるものではない。

【0015】正極は、リチウムコバルト複合酸化物 ( $\text{LiCoO}_2$ ) と導電剤としてのカーボン粉末および結着剤としてのフッ素樹脂粉末とを90:3:7の重量比で十分混合したのち、加圧成型したものである。負極は、黒鉛粉末と結着剤としてのフッ素樹脂粉末とを91:9の重量比で十分混合したのち、加圧成型したものである。

【0016】図1は、本発明の実施例電池の縦断面図である。この図において1は、耐電解液性のステンレス鋼板を打ち抜き加工した正極端子を兼ねるケース、2は1と同様のステンレス鋼板を打ち抜き加工した負極端子を兼ねる封口板であり、その内壁には負極3が当接されている。5は有機電解液を含浸したポリプロピレンからなるセパレーター、6は正極である。電池は、正極端子を兼ねるケース1の開口端部を内方へかしめ、ガスケット4を介して負極端子を兼ねる封口板2の外周を締め付けることにより密閉封口している。

【0017】有機電解液には、スルホランとジメチルスルホンとを体積比1:1で混合した有機溶媒に、六フッ化リン酸リチウムを1モル/リットルの濃度で溶解したものを用いた。電池には、上記電解液を約150 $\mu\text{l}$ 注液した。

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【0018】この電池寸法は直径20mm、高さ2mmである。本発明電池を(A)とした。上記実施例において、ジメチルスルホンの代わりにそれぞれエチルメチルスルホンおよびジエチルスルホンを用いたことの他は本実施例と同様の構成とした本発明の電池を(B)および(C)とした。

【0019】さらに比較のために、エチレンカーボネートとジエチルカーボネートとの混合物(体積比1:1)を用いたことの他は、本発明の電池と同様の構成とした比較電池を(A')とした。

【0020】次に、温度60℃の恒温槽中にて、これらの電池を2.0mAの定電流で、端子電圧が4.2Vに至るまで充電して、つづいて、同じく2.0mAの定電流で、端子電圧が2.7Vに達するまで放電する充放電サイクル寿命試験を300サイクルおこなった。各電池の充放電サイクルの進行にともなう放電容量の変化を図2に示す。

【0021】図2の結果から明らかなように、ジオキシドチオフェンと非環状スルホンとの混合溶媒を用いた本発明電池(A)、(B)および(C)は比較電池(A')に比べ充放電サイクルの進行にともなう放電容量の低下が小さい。

【0022】なお、上記実施例では、ジオキシドチオフェンとしてスルホランを用いる場合を説明したが、3-メチルスルホランやスルホランと3-メチルスルホランとの混合溶媒を用いることができる。

【0023】上記実施例では、ジオキシドチオフェンと非環状スルホンとを体積比で1:1で混合した場合を説明したが、特に限定されない。

【0024】これらの非環状スルホンのジオキシドチオフェンに対する添加量は、両者の含量に対して10~60体積%が望ましい。なぜならば、非環状スルホンの含有率が10体積%未満の場合は、凝固点の高いスルホランを用いる場合電解液が低温で凝固しやすくなり、一方、誘電率の低いスルホン化合物の含有率が60体積%を越えると電解液のイオン導電率が低下するためである。

【0025】また、本発明で使用されるスルホン化合物としては、例えばジメチルスルホン、エチルメチルスルホン、ジエチルスルホンなどの少なくとも1種以上を用いることができるが、なかでもジメチルスルホンがイオン導電率の点で、エチルメチルスルホンが低温性能の点で最も望ましい。

【0026】さらに上記実施例において、正極活物質としてリチウムコバルト複合酸化物を用いる場合を説明したが、特に限定されない。二硫化チタン、リチウムニッケル複合酸化物 ( $\text{LiCoO}_2$ ) をはじめとして二酸化マンガン、スピネル型リチウムマンガン酸化物、 ( $\text{LiMnO}_4$ ) 五酸化バナジウムおよび三酸化モリブデンなどの種々のものを用いることができる。

(4)

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【0027】本実施例では、有機溶媒にジオキシドチオフェンと非環状スルホン化合物との混合系を用いる場合を説明したが、従来リチウム電池で用いられている有機溶媒を第3成分として添加して用いることができる。例えば、 $\gamma$ -ブチロラクトン、メチルフォルメートなどのエステル溶媒、エチレンカーボネートなどの環状カーボネート溶媒、1, 2-ジメトキシエタン、テトラヒドロフランなどのエーテル溶媒、ジメチルカーボネート、エチルメチルカーボネート、ジエチルカーボネートなどの鎖状カーボネートなどがあげられる。

【0028】電解質としては、過塩素酸リチウム、六フッ化砒酸リチウム、四フッ化ホウ酸リチウム、トリフルオロメタンスルホン酸リチウム、フルオロ硫酸リチウムなどの1種以上を用いることができる。

【0029】なお、前記の実施例に係る電池はいずれもコイン形電池であるが、円筒形、角形またはペーパー形電池に本発明を適用しても同様の効果が得られる。

【0030】

【発明の効果】上述したごとく、リチウムの吸蔵・放出

6

が可能な炭素材料からなる負極と、正極と、溶媒と溶質からなる有機電解液とを備える電池において、前記溶媒にジオキシドチオフェンと非環状スルホンとの混合物を用いることで、この種電池の問題である充放電サイクルの進行にともなう放電容量の低下を有効に抑制できるものであり、その工業的価値は極めて大である。

【図面の簡単な説明】

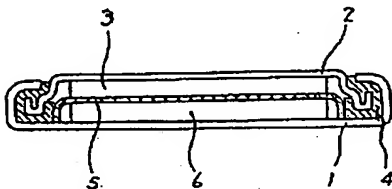
【図1】有機電解液二次電池の一例であるボタン電池の内部構造を示した図である。

10 【図2】試験電池の充放電サイクルの進行にともなう放電容量の変化を示した表である。

【符号の説明】

- 1 電池ケース
- 2 封口板
- 3 負極
- 4 ガスケット
- 5 セパレーター
- 6 正極

【図1】



【図2】

